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Understanding the behavior of 5f electrons remains an unrealized ambition of condensed matter physics [1,2]. Recently, there has been a large amount of interest in the actinides, particularly plutonium, driven by the complex and intriguing behavior of Pu and several of its compounds [3-5]. This has prompted both theoretical and experimental investigations of 5*f* metals and compounds. Of the different allotropes of Pu, the δ-phase is of particular interest because of the high symmetry crystal structure and the stability of the phase to low temperatures when alloyed with small amounts of trivalent elements. Consequently much of the recent experimental and theoretical work has focused on this allotrope. From an experimental point of view, the reactivity and radioactivity of Pu, and the complexity of the phase diagram, make it exceedingly complicated to collect high-quality data. Investigations of these complex behaviors all point back to being caused by the intriguing interplay of the various electron states and in particular the behavior of the 5*f* states. While there are a number of ongoing experimental efforts directed at determining the occupied electronic structure of Pu, there is essentially no experimental data on the unoccupied electronic structure of Pu. We aim to determine the conduction band (unoccupied) electronic structure of Pu and other actinides in a phase specific fashion and emphasizing bulk contributions by using Nano-focussed Bremstrahlung Isochromat Spectroscopy (nBIS).

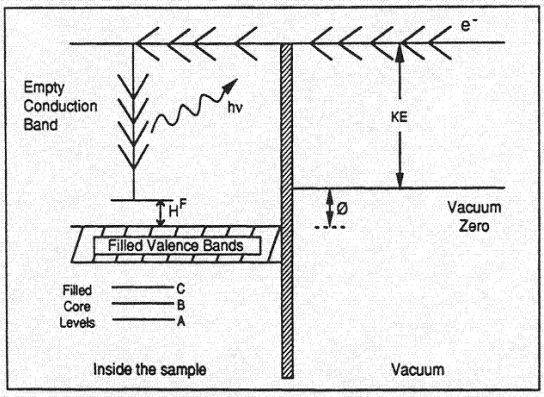

Figure 1. Schematic of the Inverse Photoemission process.

Bremstrahlung Isochromat Spectroscopy (BIS) is the high-energy variant of inverse photoelectron spectroscopy (IPES: electron in, photon out), which is essentially the time reversal of photoelectron spectroscopy (photon in, electron out). IPES can be used to follow the dispersion of electronic states in ordered samples. Owing to its low energies, IPES is usually very surface sensitive. However, by working at higher energies (>200 eV), we will sample preferentially for bulk properties, downgrading the impact of

surface effects. Thus, from BIS, we would have a direct measure of the conduction band or unoccupied electronic structure of the bulk Pu.

Our first consideration is the electron source. Laboratory IPES experiments are generally carried out using electron guns, however, given the lack of availability of single crystals of plutonium, we have decided on a methodology that will allow us to identify crystalline grains within polycrystalline samples. With this in mind we have purchased a JOEL 6300 scanning electron microscope (SEM). The SEM will give us the ability to image our sample with less than micrometer resolution and thereby pick out single crystal grains (which are of the order of >10's of μm). The microscope also provides electrons from 200- 20,000 eV in energy which we will use to excite photons for detection. The microscope and an image taken with it of gold particles on graphite are shown in Figure 2.

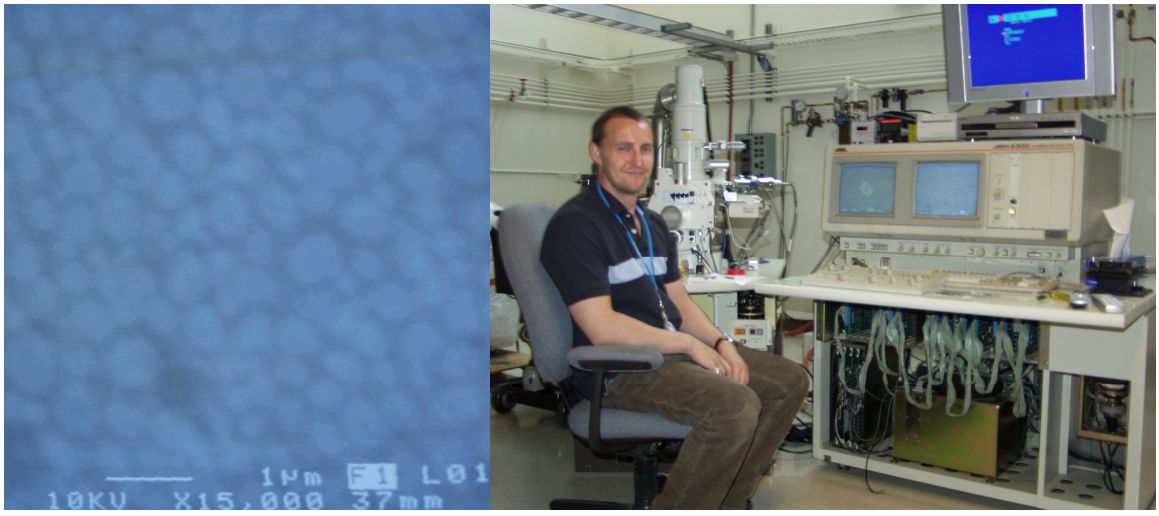

Figure 2. Image of Au particles on graphite (left panel) from JOEL 6300 SEM (right panel).

To maintain the ultra high vacuum (UHV) environment required for BIS experiments the column of the SEM will be removed and fitted to a UHV chamber specifically designed for the experiment. The column itself houses a number of O ring seals that normally would only achieve a high vacuum (> 10^{-7} Torr), but we hope to overcome this by the use of UHV greases and "aggressive" differential pumping. Though we will strive to achieve the best vacuum possible the fact that we plan to carry out the nBIS experiments at above 200 eV should mean we are less sensitive to surface contamination than standard BIS experiments.

The SEM images will give us some information on the phase of the crystallite that we are looking at, but to further elucidate this we plan on adding an Electron Back Scatter Detector (EBSD) to the system. This will allow us to take Kikuchi patterns and allow us to use a similar approach as successfully utilized for Transmission electron microscope (TEM) images and diffraction patterns as shown in the left hand panels of Figure 3 [6]. We hope to use a similar methodology utilizing the SEM and Kikuchi

patterns which, like diffraction patterns, will give us enough information to identify specific crystal phases. Kikuchi patterns taken on gallium stabilized delta plutonium by C.Boehlert et al [7] are shown in the 2 right hand panels of Figure 3.

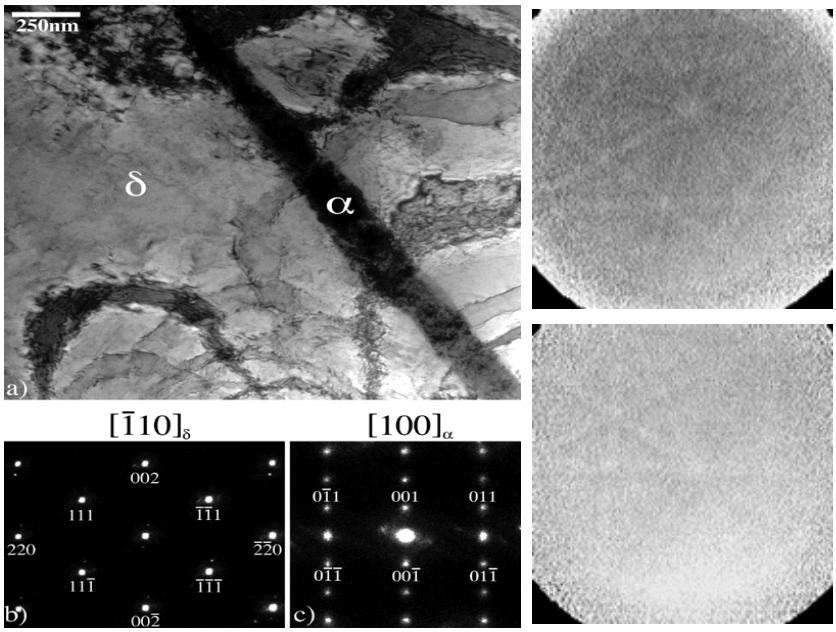

Figure 3. TEM image of Pu sample along with diffraction data (3 left panels), and Kikuchi patterns from crystalline grains in a gallium stabilized delta plutonium sample (2 right panels)

Analysis of the photons emitted from the sample will be with a Gammadata Scienta XES 350 soft X-ray spectrometer. It is a grazing incidence spectrometer covering a wide energy range, 50 -1000 eV, at high resolution and sensitivity. The instrument is flange-mounted and has an optical axis that is easily adjusted to the excitation source. The optical arrangement consists of a variable entrance slit, two moveable shutters for grating selection, three spherical gratings, and a 2-D detector that can be moved in a three-axis coordinate system. The XES 350 has a common entrance slit and a detector that can be aligned to the focal curve (Rowland circle) of the selected grating. Since the attenuation length of photons in this energy range is typically hundreds of nanometers, the method is inherently bulk sensitive.

We will mount our samples on a standard surface science high precision manipulator mounted horizontally into the vacuum chamber. In this way the azimuthal rotation of the sample manipulator will act like a “turntable” allowing us to turn the sample towards our photon analyzer or our EBSD system. We hope that once we find a good grain within the sample that we will be able to position the sample in such a way as to take both a Kikuchi pattern and an nBIS spectra at the same position.

As previously mentioned there are several ongoing efforts at obtaining the occupied density of states for Plutonium via photoemission, X-ray absorption and electron energy loss spectroscopy (EELS) [8-10] and these, as very direct measurements, have been used to benchmark the success of various theoretical calculations. While the calculations each seem to be able to explain some of Plutonium's interesting behavior, none of them appear to be able to tell the full story. As can be seen in the calculations below in Figure 4 there is a lot of information above the Fermi edge (the vertical line at zero). We hope to provide the unoccupied density of states for comparison to this information to help further benchmark the calculations and elucidate the electronic structure of Plutonium.

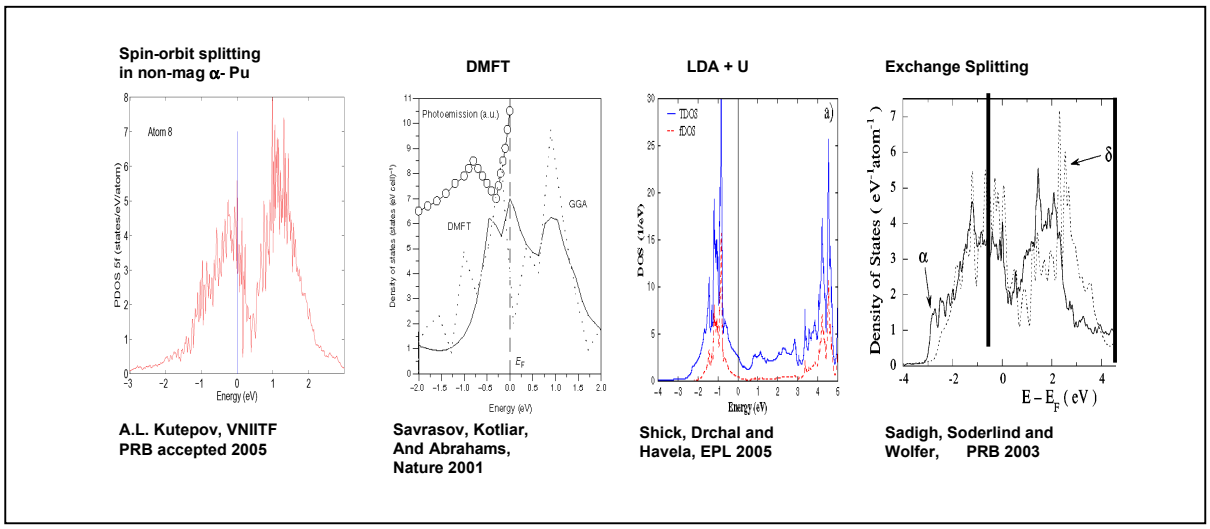

Figure 4. A small selection of electronic structure calculations for delta Pu

Between the resolution of our analyzer, and the stability of our electron source (in which we will use a BaO filament rather than the standard Tungsten) we would expect to have an overall experimental resolution of ~0.5eV. As can be seen from Figure 4 this should allow our data to be used as a benchmark to distinguish the success of these calculations.

In the literature experimental work has been reported on the "Unoccupied density of states of Th and U from Bremstrahlung Isochromat Spectroscopy (BIS)"[11]. This showed excellent agreement with theoretical studies on "Occupied (neg energies) and unoccupied (pos energies) 5f Density of States of Th and U" [12]. The experimental results are shown below in Figure 5.

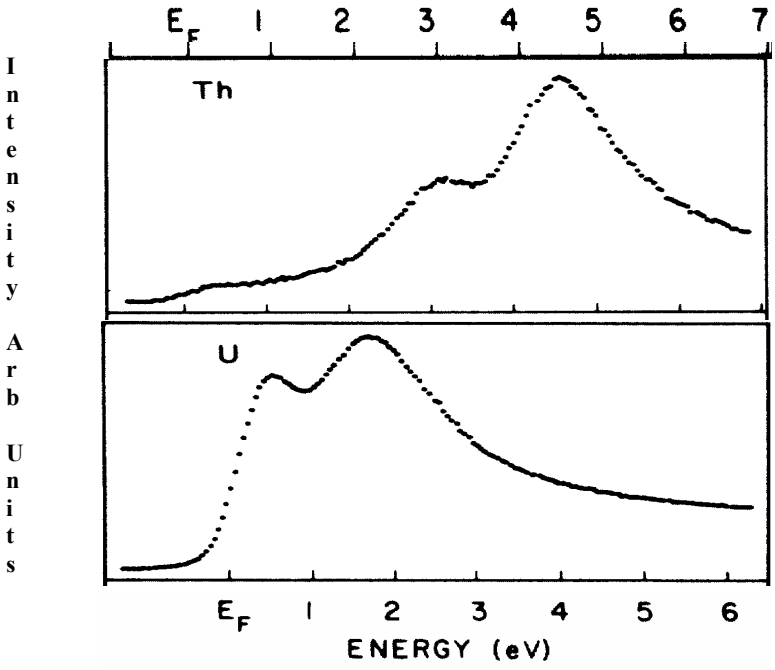

Figure 5. Experiment from Y.Baer and J.K.Lang.

We have calculations performed by A. L. Kutepov [13] which also agree well with the data of Baer and Lang for Th and U, and hope to be able to match his calculations with nBIS for Pu. Kutepov's calculations are shown in Figure 5 with the red line showing the raw calculation and the black line showing the calculation multiplied by an inverse Fermi function and smoothed to represent the approximate resolution that our experiment is expected to achieve.

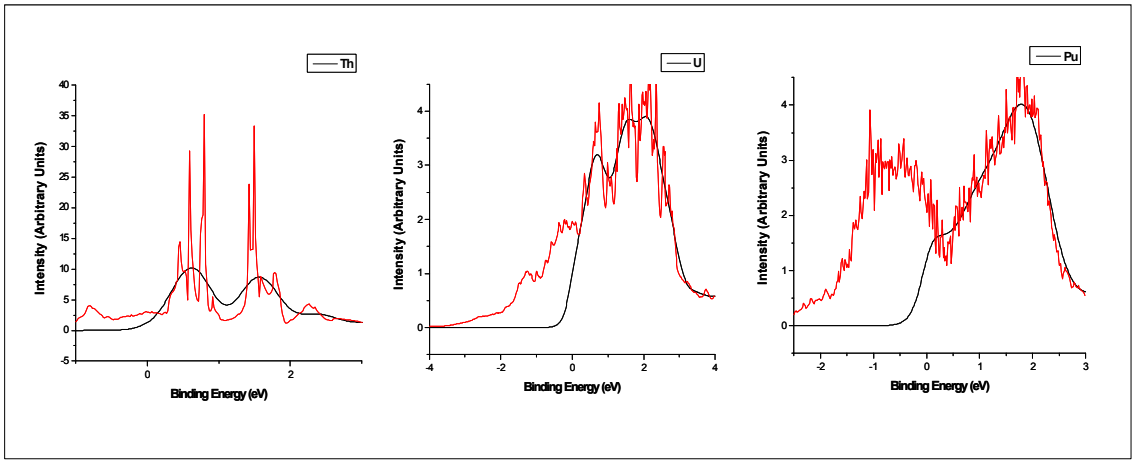

Figure 5. Calculations by A.L.Kutepov of the electronic structure for Th, U and Pu (in each case the alpha phase). The raw calculations are in red, and the calculation multiplied by an inverse Fermi function and smoothed to our likely experimental resolution is represented by the black line.

Obtaining a phase specific BIS spectra will present a significant step forward in benchmarking the theoretical effort to characterize the electronic structure of Pu.

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